

SHORT COMMUNICATION

Co-occurrence of Boundary and Resonance Ejection in a Multiplexed Rectilinear Ion Trap Mass Spectrometer

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A method is reported for evaluating ion trap mass analyzers by selection of operating conditions under which both boundary and resonance ejection peaks occur in a single mass scan. The choice of frequency and amplitude of the auxiliary waveform applied for resonance ejection can be such as to produce a resonance ejection mass spectrum with unit resolution or, under selected conditions, signals attributable to both boundary and resonance ejection in a single mass scan. The contrasting mass resolution associated with these two ejection processes is evident in these data. The co-occurrence of the two ejection phenomena is ascribed to the effects of higher-order fields; it is more marked in some rectilinear ion traps (RITs) than in other nominally identical devices, leading to the possibility of using it to compare individual mass analyzers in multiplexed instruments. The method is used to compare multiple ion traps driven by the same RF signal in a fully-multiplexed mass spectrometer, composed of parallel ion source/mass analyzer/detector channels each housed in one quadrant of a specialized vacuum chamber. (J Am Soc Mass Spectrom 2006, 17, 56–59) © 2005 American Society for Mass Spectrometry

The superposition of higher-order components (or multipoles) upon the main quadrupole potential of an ion trap is both unavoidable and, when properly engineered, advantageous to analytical performance. Truncated electrodes and electrode apertures produce nonlinear fields, including local field imperfections in the region of the electrodes, which affect the motion of ions, especially those with large excursions from the center of the ion trap as occurs just before ion ejection. The nature and magnitude of the higher-order contributions to the field of an ion trap is primarily a result of trap geometry, including the effects of mechanical dimensions and electrode alignment.

One effect of nonlinear fields present in an ion trap of non-ideal geometry is the chemical mass shift, the premature or delayed appearance of signals for particular ions in a mass spectrum. Chemical mass shifts were apparent in early Paul traps built to the theoretical geometry $r_0^2 = 2z_0^2$ until z_0 was stretched to compensate for the multipoles imposed by apertures in the endcap electrodes [1, 2]. This phenomenon has been explained using simulation and experiment, and it is now understood that the local field imperfections affect the motion of ions nearing ejection [3, 4].

Octapolar or other contributions to the primarily quadrupolar potential of an ion trap are utilized when resonance ejection is performed at a nonlinear resonance point. The frequency used corresponds to that at which overtones from the higher-order multipoles are coincident with sidebands of the quadrupole potential. In this way, resolution can be enhanced relative to that achieved in boundary ejection [5].

For ease of fabrication and miniaturization, the cylindrical ion trap (CIT) has been utilized as a geometrically simple substitute for the hyperbolic electrode Paul trap [6–10]. To minimize the effects of higher-order field components, the dimensions of the CIT have been optimized through parallel experiments and simulations [11, 12]. Likewise, the rectilinear ion trap (RIT) was introduced as a substitute for the linear ion trap, and its geometry was optimized [13, 14]. Current geometries of both the CIT and RIT contain significant positive octapolar and negative dodecapolar components after optimization.

The four RIT mass analyzers in a multi-channel mass spectrometer were compared by examining the relative contributions of boundary and resonance ejection processes in each device. This was done using resonance ejection conditions, including frequency and amplitude, specifically selected to allow signals for both type of processes to be observed in a single mass spectrum, and it proved to be a sensitive method of distinguishing individual ion traps built to the same nominal specifications.

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Experimental

The multiplexed instrument consists of four identical sets of sample inlets, electron ionization/chemical ionization (EI/CI) sources, ion transfer optics, RIT mass analyzers, and detectors. However, the parallel channels are assembled in a single manifold and have common vacuum pumps and control electronics (LCQ Classic, Thermo Electron Corp., San Jose, CA). The ion sources and Einzel lenses are commercial components (GCQ Plus, Thermo Electron Corp., Austin, TX), as are the detector assemblies (model 397, Detector Technologies, Palmer, MA). Following ionization (0.2 ms), ions enter the RIT axially through a hole in the endcap electrode and, as the amplitude of the drive RF is increased linearly to perform a mass-selective instability scan, the trapped ions are ejected radially through slits in the x electrodes and impinge upon a dynode/multiplier assembly for detection. Simultaneous acquisition of mass spectra from each of the four channels utilizes a National Instruments PCI DAQ card and a custom program written with LabVIEW software. A more detailed description and characterization of this novel instrumentation will be published later [15].

Each RIT is composed of four rectangular electrodes, 50 mm long. The x electrodes have centered slits 29 mm long and 1.0 mm in width for radial ion ejection. The half-distance between x electrodes (x_0) is 5.0 mm while that between y electrodes (y_0) is 4.0 mm. The closest edges of the x and y electrodes are separated by 1.6 mm. A space of 1.6 mm from each end of the rectangular electrodes is a planar electrode, 0.79 mm in thickness with a centered aperture 3.0 mm in diameter, for axial ion injection along the z axis of the mass analyzer. All electrodes were precision machined in-house from type 316 stainless steel with resulting tolerances of $+0.07/-0.1$ mm for the x_0 and y_0 dimensions of the assembled devices.

The drive RF (1.489 MHz) was applied to the four rectangular electrodes of the RIT, 180° out-of-phase between the x and y pairs, to cause ions to be trapped in the xy plane by the primarily linear electric field. The scan rate used was 2885 Th/s (1 Th = 1 Da/charge) [16]. In addition, a resonance ejection waveform was applied to the x electrodes in a dipolar fashion. For these experiments, the frequency and amplitude (V_{AC}) of the resonance ejection waveform were varied. However, both remain constant for the duration of the duty cycle. The DC potential (+100 V) was applied to each of the planar electrodes to create a potential well in the axial direction during cooling and mass analysis. Helium was used as buffer gas.

Results and Discussion

The mass spectrum of 1,3-dichlorobenzene recorded using one of the RIT mass analyzers with a resonance ejection q_x value of 0.81 and $V_{AC} = 1.32 V_{pp}$ shows two sets of strong signals for the molecular ion. One is due

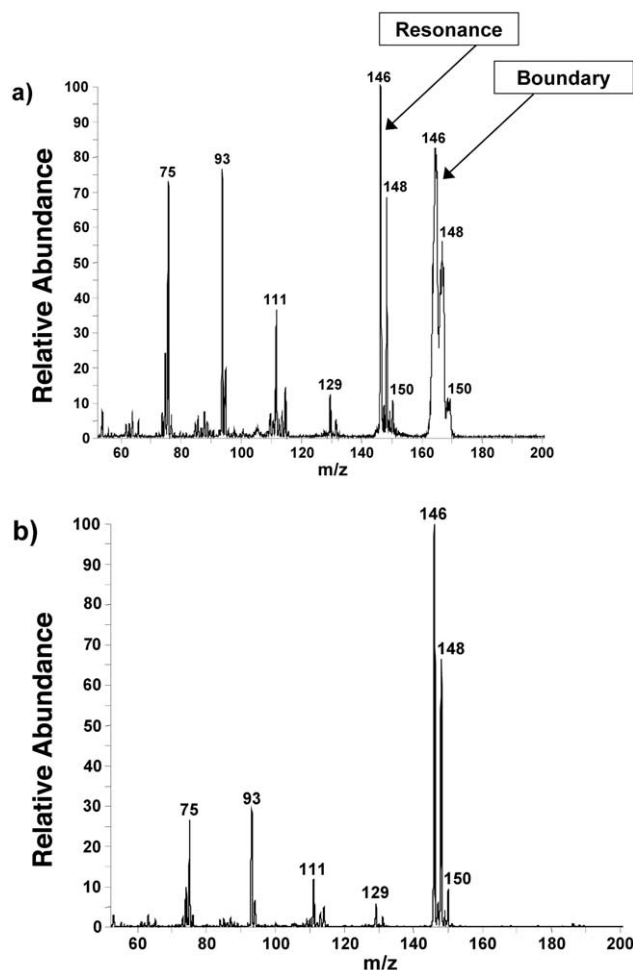


Figure 1. Mass spectra of 1,3-dichlorobenzene obtained using an RIT mass analyzer with resonance ejection at $q_x = 0.81$. The auxiliary waveform is applied to the x electrodes in a dipolar fashion with constant amplitude (V_{AC}) during the RF scan, (a) $V_{AC} = 1.32 V_{pp}$ and (b) $V_{AC} = 2.78 V_{pp}$. In (a) the characteristic 9:6:1 Cl_2 isotopic distribution occurs for the molecular ion ejected by resonance and boundary ejection processes in a single scan. In (b) the resonance ejection amplitude is sufficient for ejection of all ions to occur at the resonance point

to boundary ejection and the other to nonlinear resonance ejection (Figure 1a). Both sets of peaks show the characteristic 9:6:1 Cl_2 isotopic distribution, and the data also illustrate the contrasting mass resolution associated with each ejection process. The improved resolution associated with resonance as opposed to boundary ejection has long been known [17]. Note that the same RIT which gives equal height boundary and resonance ejection signals is capable of being operated so as to produce unit resolution resonance ejection mass spectra, but without any contribution from boundary ejection (Figure 1b). This is achieved by using a resonance ejection amplitude ($V_{AC} = 2.78 V_{pp}$) that is sufficient for ejection of all ions to occur at the nonlinear resonance point.

When the AC amplitude is insufficient for resonance ejection of all ions at a given scan speed, some molec-

ular radical cations remain trapped and are ejected at the boundary of the Mathieu stability diagram but with lower resolution than those ejected at the resonance point. Though not as apparent in Figure 1, fragment peaks were also distributed between resonance and boundary ejection processes under the appropriate conditions. A systematic investigation of the effect of the resonance ejection frequency, performed to evaluate nonlinear resonance points, showed multiple resonances including a strong resonance at q_x 0.78–0.81 ($\beta_x = 0.66$ –0.70).

From the discussion so far, it is possible to find operating conditions in which ejection due to higher-order field components (nonlinear resonance ejection) can be referenced to the amount of ejection due to normal boundary ejection. This capability might be of particular interest in the case of multiplexed mass spectrometers, since it allows direct comparison of the individual mass analyzers by performing, in all channels simultaneously, the same evaluation experiment with appropriately chosen resonance ejection frequency ($q_x = 0.81$) and amplitude ($1.32 V_{p-p}$). When this simple test is done, a screen capture of the four-channel data (Figure 2a) reveals a difference in the quality of the mass spectrum obtained from Channel 4 compared with that from the other three channels. (Note that the m/z axis is not properly calibrated in these data capture outputs.) Further comparisons over a range of q_x values showed that Channel 4 required a larger AC amplitude for resonance ejection than Channel 2 at all values of ejection q_x considered. Increasing V_{AC} to $2.78 V_{p-p}$ produced four equivalent spectra, each with unit resolution (Figure 2b) indicating that this amplitude is sufficient for ejection of all ions to occur at the nonlinear resonance point. However, it should be noted that the resolution of Channel 4 is somewhat better than that of Channel 2.

When operated with the same RF and auxiliary AC system, the individual ion traps theoretically have the same voltages and phases of these waveforms applied simultaneously. It is hypothesized that the RIT mass analyzers in the multiplexed instrument differ subtly in their higher-order field contents, a result that might be the consequence of differences in mechanical dimensions or misalignment of the parallel electrodes. This conclusion was strengthened by an experiment in which the signals to two pairs of RIT analyzers were switched (1 and 4, and 2 and 3). The results were substantially unchanged, and the differences being measured are believed to be inherent to the individual mass analyzers. However, further experiments would be required to completely reject system assembly or electrical factors.

The rectilinear ion trap (RIT) used as the mass analyzer in the novel multi-channel instrument is at the same time a high-performance ion trap (providing much better than unit mass/charge resolution, as shown here) and a device in which the quadrupole fields are of poor quality due to simplified geometry. This latter point is evident from the large signals that can be recorded due to nonlinear fields under appro-

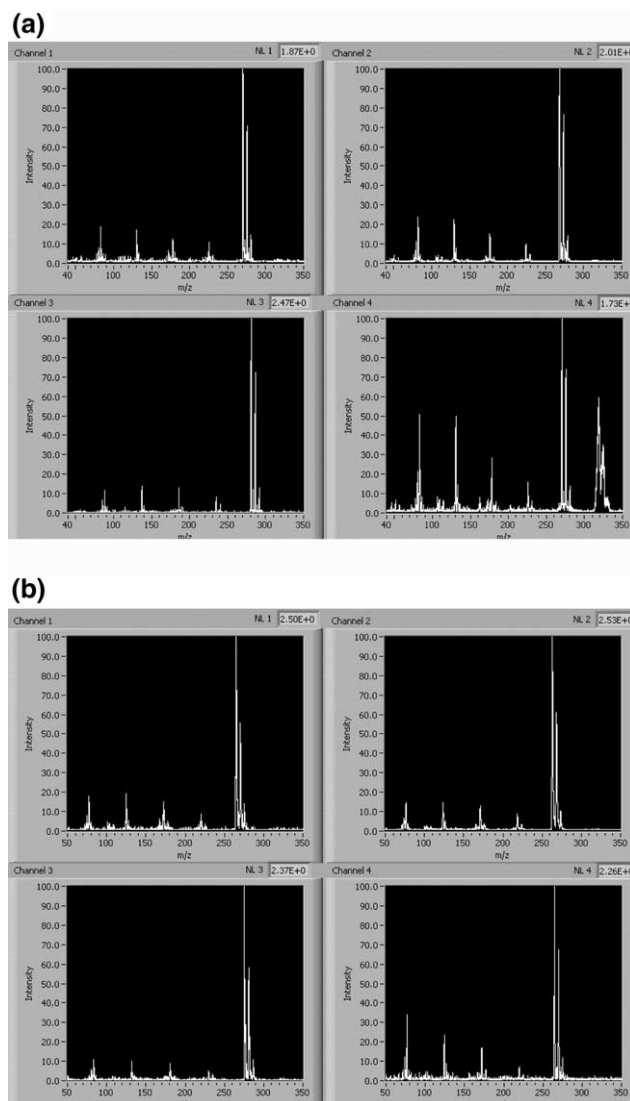


Figure 2. (a) Appropriately chosen resonance ejection frequency ($q_x = 0.81$) and amplitude ($V_{AC} = 1.32 V_{p-p}$) yield four-channel data from a multiplexed RIT mass spectrometer which reveal a difference between the performance of the mass analyzer in Channel 4. (b) Increasing V_{AC} to $2.78 V_{p-p}$ produces four equivalent spectra. Note that the m/z axes are not properly calibrated. Also note that both sets of spectra show comparably high mass resolution

priately chosen conditions. In spite of this, the differences in performance of the four RITs of the multiplex instrument are small when using typical, optimized operating conditions.

Conclusions

The data of this communication illustrate the contrasting resolution associated with boundary and resonance ejection and more importantly, they provide a subtle method of distinguishing nominally identical mass analyzers operated from a single power supply by the dramatic differences in the mass spectra recorded under appropriate operating conditions. The fact that the

ejected ion signal associated with resonance energy uptake can be referenced to the amount of ejection attributable to normal boundary ejection makes this a sensitive measure of higher-order field contributions although the applications of this subtle measurement remain to be more fully developed.

The different rectilinear ion traps in a multiplex mass spectrometer are readily distinguished by this experiment, in which selection of operating conditions is made so that both boundary and resonance peaks occur in a single mass spectrum. A preliminary conclusion of these findings is that the higher-order field contents of the RITs are unequal due to geometric differences. Simulations and further experiments are required to determine whether the higher-order field effects are due to differences in the x_o/y_o ratio, misalignment of the parallel electrodes, the absence of slits in the y electrodes, or the surface characteristics of the slits present in the x electrodes.

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